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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Vuorinen et al	**Atty. Ref.: 30-336**
Serial No. 08/542,646	**Group: 1303**
Filed: October 13, 1995	**Examiner: Alvo**

For: Method of Treating Cellulose Pulp

* *

Honorable Commissioner of
Patents and Trademark
Washington, DC 20231

EVIDENTIARY DECLARATION OF TAPANI VUORINEN

Sir:

I, Tapani Vuorinen, hereby say and declare:

1. My curriculum vitae is attached hereto as Exhibit A. I am one of the co-inventors of the above-identified application.

2. The Lachenal et al reference (1982 International Bleaching Conference, pages 145-151) of record in this application describes a combination of an acidic treatment with a subsequent peroxide bleaching stage. The charge of sulfuric acid in the acidic stage is 8% on pulp which, according to the authors, corresponded to a pH~2. In reality the pH must have been lower. The pH can be evaluated from the charge of the acid when the anionic charge of the pulp is approximately known (Laine et al, Colloids and Surfaces, A, 88, 1994, 277-287). Such a calculation shows that the pH corresponding to a 2% charge of sulfuric acid is ~1.5. At the 12% pulp consistency pH ~2.0 would be obtained with a 1.3% charge of sulfuric acid.

3. Lachenal et al show that a major effect of their acidic treatment, irrespective of its temperature, is a reduction in manganese content of the pulp. Because manganese catalyzes decomposition of peroxide, a better bleaching result was obtained with the acidic pretreatment. It may be noted that peroxide bleaching is currently widely applied for bleaching of kraft pulps but an acidic pretreatment is not generally used for the removal of manganese ions. This is mainly because efficient manganese removal requires a high acid charge and a low pH (≤2). Instead of a treatment with acid, pulps are usually treated with complexing agents in order to remove manganese or other heavy metal ions before a peroxide bleaching stage.

4. Lachenal et al also show that the efficiency of the acid treatment is increased when it is performed at elevated temperatures. Experiments were done at 50, 70, and 90°C. In the conclusions the temperature range was restricted to 60-80°C. No specific reason was given for why a treatment at 90°C was not in the preferred range, however my understanding is that at 90°C the high acid charge, corresponding to a pH of ~1.5, decreases the viscosity of the pulp dramatically. The strength properties become poor which makes the treatment under these conditions impractical. In fact, Lachenal et al describe viscosities and strength properties only for pulps treated with the acid at 70°C where the hydrolysis of cellulose must have been much less extensive.

5. The above-identified application relates to a method for selectively hydrolyzing hexenuronic acid groups in pulps. Before the invention the existence and importance of hexenuronic acid as related to bleaching chemicals was not, to my knowledge, known in the art. Hexenuronic acid groups consume bleaching

chemicals, bind heavy metal ions, cause brightness reversion, and form a major oxalate source in pulp bleaching. For these reasons it is often advantageous to remove the hexenuronic acid groups before final bleaching.

6. They hydrolysis of hexenuronic acid groups follows an exceptional reaction kinetics. The reaction rate gets its maximum value at pH 3-4 (Vuorinen et al, 1996 International Pulp Bleaching Conference, 48-51). The reaction cannot be speeded up much by lowering the pH further to 1.5-2. In order to remove most of the hexenuronic acid groups a relatively high temperature and long treatment time is necessary. Typically the temperature is over 85°C, and preferably at least 90°C, and the treatment time several hours.

7. In 1995 I, with the cooperation of others, carried out extensive studies on how the selective hydrolysis of hexenuronic acid groups could be implemented in bleaching of kraft pulps. We were fully aware of the negative effects of too low a pH and therefore we were also looking for an optimum pH for treatment. The viscosity decreased least at pH 3-4, preferably 3-3.5 (depending on the pulp). Since these studies I have continuously been involved in development and application of the selective hydrolysis stge. My experience is that the viscosity of pulp is really a factor that must be under control although the hydrolysis is carried out at pH 3-3.5.

8. A significant difference between the acidic treatments of Lachenal et al and the invention is illustrated with the following examples. In Table 1 (appended as Exhibit B) softwood kraft pulp (kappa number 25.4) was treated at pH 2 (0.01 M sulfuric acid) and 3.5 (formiate buffer) at 90°C. Both treatments reduced the kappa number by 3.6-3.7 units (Table 1). Simultaneously 32-33 meq/kg of hexenuronic

acid groups were removed. This reduction corresponds to a 3.4 units decrease in the kappa number (Vuorinen et al, 1996 International Pulp Bleaching Conference, 43-51). Thus, the kappa number reductions in the acidic stages were solely caused by reductions in the hexenuronic acid content of the pulp. As Table 1 shows, at pH 3.5 the viscosity was decreased but at pH 2 it dropped dramatically. This example shows that the treatment described by Lachenal et al at 90°C is impractical. A key is that the pH of the acidic stage must be high enough in order to prevent the hydrolysis of cellulose.

9. In a second example (Table 2, Exhibit C hereto) an oxygen bleached hardwood kraft pulp was treated at pH 1.5 (2% sulfuric acid on pulp) and 3.5 (formiate buffer) at 90°C. The kappa number reduction was in both cases 4.2-4.5 units (Table 2). Because the decrease in the hexenuronic acid content was 29-31 meq/kg, a small fraction of the kappa number reduction could be caused by hydrolysis of lignin structure. The viscosity losses were moderate at pH 3.5 but at pH 1.5 the viscosity again dropped dramatically. Thus, the conclusions are the same as from the previous example.

10. In a third example (Table 3, Exhibit D), unbleached and oxygen bleached hardwood kraft pulps were treated at pH 2 (1.3% sulfuric acid on pulp) and pH 3.5 (formiate buffer or adjustment with sulfuric acid) at 70 and 90°C. After the treatments the pulps were neutralized and treated with a complexing agent (0.2% EDTA on pulp) in order to remove heavy metal ions. Finally the pulps were bleached with alkaline hydrogen peroxide (3% on pulp) for two hours at 90°C. As Table 3 shows, removal of hexenuronic acid groups at 70°C was limited to 2.4-6.5

meq/kg. The kappa number reduction under the same conditions was 0.7-1.1 units. At 90°C the removal of hexenuronic acid groups was much more extensive which also resulted in a lower kappa number after the acidic stage. None of the acidic pretreatments improved lignin removal in the peroxide stge. This can clearly be seen by comparing the kappa number difference before and after the peroxide stage. Thus, at least in this case, the effect of the acidic pretreatment was restricted to the removal of hexenuronic acid groups.

11. A last example (Table 4, Exhibit E) shows that the effects described by Lachenal et al for an acidic pretreatment at pH ~ 2 at 60-80°C lack generality. To the contrary, the selective hydrolysis described according to the invention gives effects that can be predicted from the hexenuronic acid content of the pulp.

12. In conclusion, the acidic treatments described by Lachenal et al and the invention are clearly different. In the first case the treatment is optimally at pH ~2 at 60-80°C. The low pH prevents practical treatments at higher temperatures where the removal of hexenuronic acid groups becomes prominent. The bleaching result depends on the pulp. In some cases the acidic pretreatment gives no advantage.

13. The acidic treatment of the invention is optimally performed at about pH 3-4 and above 85°C, preferably at or above 90°C. The effect of the treatment is based on the removal of hexenuronic acid groups and is thus predictable from their content in the pulp.

14. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be

true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Tapani Vuorinen

Tapani Vuorinen

Date: March 6, 1997

CURRICULUM VITAE

Personal data

Full name: Vuorinen, Jouko Tapani
Date and place of birth: 22 September 1957, Turku
Parents: Lauri Vuorinen and Aila Vuorinen, b. Kyrö
Married: 1985 with Kristiina Virtanen
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Education

Matriculation Examination, Uusikaupunki High School, 29 May 1976
Master of Science in Technology, Helsinki University of Technology, 29 August 1980
Doctor of Technology, Helsinki University of Technology, 30 August 1988

Professional appointments

Assistant in Wood Chemistry, Helsinki University of Technology, 1.1.1980-31.7.1991
Senior Research Fellow, Academy of Finland, 1.8.1991-31.3.1996.
Docent in Organic Chemistry, Turku University, 2.3.1994-
Docent in Forest Products Chemistry, Helsinki University of Technology, 1.6.1994-
Associate Professor in Forest Products Chemistry, Helsinki University of Technology, 1.4.1996-

International activities

University of Notre Dame, USA, visiting scientist, 22.8.1988-28.2.1989, 18.9.-19.11.1989.
International Carbohydrate Organization, member, 1994-

Other activities

Secretary, National program on carbohydrates in process technology (Technology Development Centre Finland), 1993-
Lecturer, Turku University
- Synthetic organic and bio-organic chemistry: synthetic carbohydrate chemistry, 1993
- Wood Chemistry, 1994

Lecturer, Helsinki University of Technology
- Methods in chemistry of forest products technology, 1993-
- Chemistry of lignin and its properties in pulping processes, 1993-

Memberships in scientific societies

Finnish Chemical Society, 1980-
American Chemical Society, Division of Carbohydrate Chemistry, Division of Agricultural & Food Chemistry, Division of Cellulose, Paper & Textile Chemistry, 1989-

Awards and honours

Honorary award of young scientists, Finnish Chemical Society, 1980
Special mention, Technology Development Centre Finland, National program on carbohydrates in process technology, 1993
Honorary mention, National Blue Globe contest for inventions promoting clean environment, 1996

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March 3, 1997

Tapani Vuorinen

EXHIBIT B

Table 1. Effect of acidic treatments on the properties of a softwood kraft pulp. ΔHexA denotes the amount of hexenuronic acid groups removed in the acid treatment. Treatments were carried out at 3 % pulp consistency.

pH	Time (h)	Kappa number	Viscosity (ml/g)	ΔHexA (meq/kg)
-	-	25.4	1166	-
2	1	22.5	1074	18.7
2	2	22.1	962	25.7
2	4	21.7	869	32.8
3.5	1	23.3	1107	13.6
3.5	2	22.8	1117	20.4
3.5	4	21.8	1069	32.2

EXHIBIT C

Table 2. Effect of acidic treatments on the properties of an oxygen bleached hardwood kraft pulp. ΔHexA denotes the amount of hexenuronic acid groups removed in the acid treatment. Treatments were carried out at 10 % pulp consistency. The pH 1.5 corresponds to a charge of 2 % of sulfuric acid on pulp.

pH	Time (h)	Kappa number	Viscosity (ml/g)	ΔHexA (mmol/kg)
-	-	11.9	1005	-
1.5	1	10.7	975	9.7
1.5	2	9.5	919	14.9
1.5	4	8.4	834	30.9
3.5	1	11.2	986	4.6
3.5	2	10.5	961	11.8
3.5	4	8.7	935	29.2

EXHIBIT D

Table 3. Effect of acidic pretreatments on peroxide bleaching of a hardwood kraft pulp. ΔHexA denotes the amount of hexuronic acid groups removed in the acid treatment. Treatments were carried out at 10 % pulp consistency. The duration of treatment was 2 hours except for the treatment at pH 3.5 at 90 °C that lasted 6 hours.

A-stage pH	A-stage temperature (°C)	Kappa number before P-stage	Kappa number after P-stage	ΔHexA (meq/kg)
-	-	15.3	8.9	-
2	70	14.6	8.3	6.5
3.5	70	14.3	8.9	5.1
2	90	12.6	6.7	27.1
3.5	90	12.3	5.9	40.0

EXHIBIT E

Table 4. Effect of acidic pretreatments on peroxide bleaching of an oxygen bleached hardwood kraft pulp. ΔHexA denotes the amount of hexenuronic acid groups removed in the acid treatment. Treatments were carried out at 10 % pulp consistency. The duration of treatment was 2 hours except for the treatment at pH 3.5 at 90 °C that lasted 6 hours.

A-stage pH	A-stage temperature (°C)	Kappa number before P-stage	Kappa number after P-stage	ΔHexA (meq/kg)
-	-	11.1	9.9	-
2	70	10.0	7.3	6.3
3.5	70	10.4	7.4	2.4
2	90	8.5	4.7	29.0
3.5	90	8.1	4.2	37.8